THE ACTION OF SILICATES

IN

THE COAGULATION OF WATER TURBIDITY

THE ACTION OF SILICATES IN THE COAGULATION OF WATER TURBIDITY

by

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INTRODUCTION

It has been found in recent years that the presence of silicates in water is an aid in coagulation. That this discovery has certain commercial applications is beyond question, but the degree to which it may be applied in the clarification of water for industrial use has not yet been determined. Quantitative data on the amount of silicates left in the water, which would greatly influence the degree of boiler scale formation, is forthcoming. The scope of this work is to study the form of silica which is an aid to coagulation, that is, whether it is ionic or or colloidal; to determine the effect of dialysis on the silicate solutions; to determine the effect of hydrogen ion concentration, and the effect of interfering ions. Inasmuch as the literature abounds in contradictions as to whether the form of the silica as found in natural waters and in silicate solutions is colloidal, dissolved (crystalloid) or ionized, the investigation of such a problem should furnish one with interesting results. The problem leads to the study of the following equilibrium

$$SiO_2 \times H_2O \rightleftharpoons SiO_2 \times H_2O \rightleftharpoons H^+ + HSiO_3 \rightleftharpoons H^+ + SiO_3$$

(Colloid) (Crystalloid)

and to the determination of the velocity of transference of colloidal silicates to other forms.

LITERATURE SURVEY

There is a variety of conflicting opinions in regard to the question of the form in which the silicates appear when in solution. Mellor (1) postulates that in the hydrogel of silicic acid it is almost certain that the water is not chemically combined with the silica and the so-called silicic acids are to be regarded as adsorption products.

Dienert and Wandenbulke (2,3) reported the fact that dissolved silica and not colloidal was responsible for the color developed in the colorimetric determination of silica. They also reported the fact that by heating the solution with sodium bicarbonate the colloidal could be converted to the dissolved form.

Recently R. W. Harman (4,5,6,7,8) in his work on sodium silicates proved the existence of the following equilibrium:

$$(\text{Colloidal } SiO_2,\ H_2O) \rightleftharpoons (\text{crystalloid } H_2SiO_3)$$

$$H_2SiO_3 \rightleftharpoons H^+ + HSiO_3^- \rightleftharpoons H^+ + SiO_3^=$$

Harman also states: "Hitherto the silica in solution has usually been regarded as wholly colloidal in nature whether a solution of an alkaline silicate or of silicic acid has been the subject of investigation."

Harman also drew the following conclusions from investigation of electrical conductivity and transport numbers:

(1) Salts corresponding to 1:1 and 1:2 mols Na_2O to SiO_2 exist in solution and the other ratios are mixtures of these with NaOH or hydrated silica as the case may be.

(2) Sodium metasilicate Na_2SiO_3 has a very high conduc-

tivity in dilute solutions. The high conductivity is undoubtedly due to the presence of the very mobile hydroxyl ion formed on hydrolysis.

(3) The fair conductance of dilute solutions points to a high degree of ionization and a fairly mobile silicate ion, while in concentrated solutions there may be either very little ionization or there may be complex or colloidal formation.

(4) The transport number of the silicate ion $SiO_3^{=}$ is 16, that of the sodium ion Na^{+} is 31. By subtracting we get the transport number of the OH^{-} as 53.

(5) Taking the transport number of an ion to be proportional to its mobility and to its concentration, this makes the mobility of the simple silicate ion equal to 70.

(6) The transport number of Na_2SiO_3 shows no evidence whatever of any complex silicate ions or of micelle formation.

(7) The values of V, the activity coefficient of Na_2SiO_3 shows that in dilute solutions practically all of the sodium exists in the active state.

(8) Contrary to previous belief the salt Na_2SiO_3 is not completely hydrolyzed even in dilute solution.

Pastma (9) investigated the coagulation of alkaline SiO_2 sols and aqueous sodium silicate. He found for $BaCl_2$ and $CaCl_2$ the coagulation concentration decreases with increasing alkalinity; for NaCl, NH_4Cl and $Al_2(SO_4)_3$ the reverse is the case. The limiting concentration for $BaCl_2$ becomes smaller and the quantity of Ba^{++} adsorbed by the precipitate becomes greater the older the solution.

E. Baschieri (10) supporting Tschermak agrees that the silicic acids cannot be "adsorption compounds" since they show discontinuous desiccation curves.

A. Grundman (11) showed that the charge of the silicic particles in an HCl solution of silicic acid changes when the sol is kept for some time.

Kenkyo Inaba (12) states that a .3% dispersion of silicic acid in water is a colloidal solution as long as the alkali concentration is less than 0.01 N. Above this alkalinity it functions as a true solution of sodium silicate.

Daelter (13) concluded from his work that ions were even present in solid silicates but that they were too firmly bound to show conductivity until the mobility was increased by raising the temperature.

J. R. Baylis (14, 15, 16, 17) who made the most recent investigations concerning the silicates says that the form of silica which gives aid to coagulation is not known definitely, though it is believed to be a colloidal hydrous silicon dioxide possessing a strong negative charge.

EXPERIMENTAL

Reagents

1. Na_2SiO_3--Sargent's - Water glass of technical grade, 40% Na_2SiO_3.
2. Na_2SiO_3-- Merck's - Water glass of technical grade, 40-42 Be^o.
3. Infusorial Earth.
4. Aluminum Sulfate - $Al_2(SO_4)_3 \cdot 18H_2O$.
5. Filter Alum - $Al_2(SO_4)_3 \times H_2O + x\ Al_2O_3$.
6. Bakers analyzed - sodium bicarbonate, potassium chromate, sodium hydroxide, calcium hydroxide, ammonium molybdate.
7. Mercks - Ferric alum.

The Determinations

The silicate solutions used were analyzed for SiO_2 content in the accepted analytical procedure (24).

The sodium can be determined as sodium chloride or sodium sulfate using the hydrofluoric acid method of Berzelius (24). The percentages obtained are given below.

	SiO_2	Na_2O
Sargent's	30.5	9.01
Mercks	29.3	9.3

This gave a $Na_2O \cdot SiO_2$ ratio of 1:3.38.

Sodium silicate solutions were prepared of 3.7% SiO_2 strength. This concentration was selected because Baylis proved this to be the optimum amount to use. I verified Baylis' work on this point. Directions given in Baylis (16) were followed. Assuming that the sodium silicate contained 30.5% of SiO_2, 123 grams of the material diluted to 1 liter will give a solution containing .037 grams of SiO_2 per ml.

Fifty ml. of the silicate solution containing .037 grams per ml. SiO_2 were diluted to about 85 ml. with distilled water. One normal H_2SO_4 was added with the aid of a burette, using phenolphthalein solution as an indicator, until the pink color of the solution disappears. The acid was added rapidly at first and then drop by drop until the time required for the pink color to reappear is 10 to 15 seconds. The solution was agitated during the addition of the acid. The amount of N/1 H_2SO_4 used was 16.55 ml. The solution was then diluted to 100 ml. A 10 ml. portion of this acid treated sodium silicate is diluted to

50 ml. with distilled water. Two or three drops of methyl orange were added to the solution, and titrated with N/30 H_2SO_4 to the same shade of color required in making alkalinity tests on water. The amount of N/50 H_2SO_4 required was 12.4 ml. The resulting solution has an alkalinity of 1240 p.p.m. expressed as $CaCO_3$.

CHAPTER I

Aluminum Sulfate as a Coagulating Agent

The purpose of the work reported in this chapter is to find the optimum concentration of alum that will give good coagulation and what conditions prove most favorable for coagulation. Aluminum sulfate and filter alum were used as coagulating agents. Filter alum was chosen as a coagulant after a few preliminary experiments were performed. Infusorial earth was used to produce the desired turbidity. An alkaline reagent such as calcium hydroxide or calcium bicarbonate was added to distilled water in conducting the experiments. The experiments were conducted in 1 liter beakers containing 500 ml. of solution. A stirring device was used which gave efficient stirring of 120 revolutions per minute. Experiments were conducted in sets of six.

The characteristics of the coagulation were divided into the following classifications:

(1) Very fine - Coagulated particles barely detectable.

(2) Fine - The particles were still small but large enough to be detectable.

(3) Medium - The particles appeared to be about .5 to .8 mm. in size.

(4) Large - Many of the coagulated particles appeared to be about 1.5 mm. in size with a large portion of them being at least 1 mm. in size.

(5) Immense - When most of the coagulated matter was included in particles over 1.5 mm. in size.

With some experience one is enabled to place the size of the particles in the proper class. At least, the classification enables one to distinguish between the different coagulations with a fair degree of accuracy.

The first experiments were designed in order to find the optimum quantity of alum necessary to give good coagulation in a reasonable length of time. The different alkaline reagents used in the first experiments were calcium hydroxide, calcium carbonate, calcium bicarbonate and sodium bicarbonate. Calcium bicarbonate was later used altogether. A carbon arc lamp was used to give constant illumination, and to enable one to identify the size of the particles readily. A Hellige comparator was used to make all pH determinations.

In table I is tabulated the size of the coagulated particles using varying concentrations of filter alum. A calcium hydroxide alkalinity of 46 p.p.m. was used in this experiment. The turbidity of the sample was 30 p.p.m. and the temperature was 24° C. In the remainder of the experiments turbidities and alkalinities are reported in terms of p.p.m. Temperatures are reported in terms of degrees centigrade. The size of the particles varies directly with the concentration of the filter alum provided the alkalinity is high enough to form the aluminum hydroxide. The pH and alkalinity at the end of the series decreases with increasing quantities of filter alum.

TABLE I

Effect of Varying the Concentration of the Filter Alum on the Size of the Coagulated Particles

ml.	Filter Alum p.p.m.	Minutes Stirring 5	10	15	20	25	Ph	Alk.
1. 2	4	very fine	medium	medium	no chg	lrg.med.	7.7	44
2. 4	8	fine	lrg.med.	lrg.med.	"	lrg.med	7.6	42
3. 6	12	fine	lrg.med	lrg.med	"	lrg.med	7.6	38
4. 8	16	low med.	lrg.med	large	"	large	7.4	34
5.10	20	large	ex. lrg	ex. lrg	"	ex lrg	7.4	34
6. 12	24	large	ex. lrg	ex. lrg	"	ex. lrg	7.2	28
7. 14	28	ex. lrg	ex. lrg.	ex. lrg	"	ex. lrg	7.0	18
8. 16	32	ex. lrg	ex. lrg	ex. lrg	"	ex. lrg	7.0	14
9. 18	36	ex. lrg	ex. lrg	ex. lrg	"	ex. lrg	6.8	10
10. 20	40	ex. lrg	ex. lrg	ex. lrg	"	ex. lrg	6.4	8
11. 22	44	lrg.med.	large	ex. lrg	"	immense	6.2	6
12. 24	48	lrg.med.	large	immense	"	immense	6.0	6

$Ca(OH)_2$ Alkalinity 46 Turbidity 30 Temperature 24

The same type of experiments were run with alkalinities of 68, 32, and 18 p.p.m. With an alkalinity of 68, good coagulation was obtained. An alkalinity of 18 did not give good coagulation, due to the low pH of the solution. The most desirable flocculation was obtained when the alkalinity was 32 p.p.m. and the turbidity was 30 p.p.m., and when the amounts of alum lie between 8 and 20 p.p.m.

Table II shows the effect of using $CaCO_3$ to give the desired alkalinity to the solution. The table shows that pH and good flocculation are closely related. A pH of about 7.2 seems to give best results. The higher concentrations of alum do not give the largest size particles. Calcium carbonate does not give as large particles as does calcium hydroxide.

TABLE II

Effect of $CaCO_3$ on Size of Coagulated Particles

	Alum	Minutes Stirring						
	p.p.m.	5	10	15	20	25	Ph	Alk
1.	0	very fine	very fine	very fine	very fine	very fine	7.6	25
2.	4	very fine	very fine	very fine	very fine	very fine	7.6	24
3.	12	very fine	fine	medium	lrg. med.	large	7.2	22
4.	20	very fine	very fine	very fine	medium	lrg. med.	7.0	20
5.	28	very fine	very fine	very fine	fine	lrg. med	6.6	16
6.	36	very fine	very fine	very fine	very fine	medium	6.3	14

$CaCO_3$ Alkalinity 25 Turbidity 30 Temperature 24

Table III shows the effect of using calcium bicarbonate to produce the desired alkalinity to distilled water. The results obtained further substantiate table II in regard to pH and alkalinity, as it affects the size of the coagulated particles.

TABLE III

Effect of using $Ca(HCO_3)_2$ on the Size of the Coagulated Particles

	Alum p.p.m.	Minutes Stirring 5	10	15	20	25	pH	Alk.
1.	0	none	none	none	none	none	7.2	32
2.	4	very fine	very fine	medium	lrg.medium	large	7.0	28
3.	12	very fine	very fine	fine	medium	lrg.med.	6.7	20
4.	20	very fine	very fine	very fine	very fine	very fine	6.4	14
5.	28	"	"	"	"	"	6.0	8
6.	36	"	"	"	"	"	6.0	4

$Ca(HCO_3)_2$ Alkalinity 32 Temperature 24 Turbidity 30

The results given in Table III show the effect of using calcium bicarbonate to produce the desired alkalinity. The results obtained further substantiate those shown in Table II in regard to pH and alkalinity and their effect on the size of the coagulated particles.

CHAPTER II

Influence of Sodium Silicate on Coagulation

The purpose of the work reported in this chapter is to prove that sodium silicate solutions do aid coagulation and in what conditions they exert their maximum aid. Sodium silicate solutions that have not been treated with sulfuric acid gave no aid to flocculation. In each experiment sodium silicate solutions were used which had an alkalinity of approximately 1240.

In order to prove that the aid to coagulation was due to the silicate ion, sodium sulfate was used in the absence of silicate. No aid to coagulation was obtained. The only effect of the $SO_4^=$ was to increase the range of coagulation to the acid side.

Table IV illustrates the effect of adding sodium silicate to different concentrations of coagulating agent. A concentration of 3.7 p.p.m. was used because Baylis (14) proved this to be the amount to use. I verified Baylis' work on this point. The table clearly shows that the addition of sodium silicate of 3.7 p.p.m. is an aid to coagulation. The floc was more adhesive in the cases where sodium silicate was used. Number 1, after stirring 30 minutes, showed very large flocs.

TABLE IV

Effect of Adding Sodium Silicate of 3.7 p.p.m. Concentration to Varying Quantities of Alum

	Alum p.p.m.	SiO_2 p.p.m.	Minutes Stirring 5	10	15
1.	8	3.7	medium	medium	no change
2.	16	3.7	medium	medium	no change
3.	24	3.7	very large	immense	no change
4.	32	3.7	very large	immense	no change
5.	40	3.7	very large	immense	no change
6.	48	0	large	large	no change

$Ca(OH)_2$ Alkalinity 46 Turbidity 30 Temperature 24

Table V illustrates the use of calcium bicarbonate instead of calcium hydroxide to produce the desired alkalinity. The SiO_2 content was constant at 3.7 p.p.m. The purpose of this experiment was to find the minimum concentration of alum which gave good flocculation with the addition of sodium silicate.

TABLE V

Effect of Using Calcium Bicarbonate with Distilled Water on the size of the Coagulated Particles

	Alum p.p.m.	SiO_2 pp.m.	Minutes Stirring 5	10	15	20	Ph	Alk.
1.	0	0	none	none	none	none	7.2	34
2.	1	3.7	very fine	fine	fine	fine	6.9	32
3.	2	3.7	very fine	fine	low medium	low medium	6.9	32
4.	3	3.7	fine	low med	medium	medium	6.8	30
5.	4	3.7	fine	medium	lrg. medium	lrg. med.	6.8	30
6.	5	3.7	medium	large	large	large	6.8	28

$Ca(HCO_3)_2$ Alkalinity 34 Temperature 24

Turbidity 30

Table VI shows the marked influence of sodium silicate on aluminum hydroxide coagulation. In the case of no. 4, the ratio of sodium silicate to aluminum sulfate was too high to give good flocculation, Baylis (15). If the ratio of sodium silicate to aluminum sulfate is greater than 1 to 3, efficient flocculation cannot be obtained, Baylis (15). Table VI also shows the use of sodium bicarbonate to produce the desired alkalinity.

TABLE VI

Effect of Sodium Bicarbonate with Distilled Water on the Size of the Coagulated Particles

Alum p.p.m.	SiO_2 p.p.m.	Minutes Stirring 5	10	15	20
1. 0	0	none	none	none	none
2. 4	0	none	fine	low medium	lrg medium
3. 10	0	none	fine	low medium	medium
4. 4	3.7	fine	fine	fine	fine
5. 10	3.7	medium	large	large	lrg medium

$NaHCO_3$ Alkalinity 40 Turbidity 30 Temperature 24° C

Table VII shows correlation between age of sodium silicate solutions, varying $Al_2(SO_4)_3$ concentration, and coagulating power. The table indicates that freshly prepared sodium silicate solutions offer no aid to coagulation. By freshly prepared solutions we mean that the solutions have not aged more than five minutes. The maximum aid develops in from 1 to 2 hours. After the sodium silicate solutions had aged for four days they still gave aid to coagulation.

TABLE VII

Relation Between Age of Sodium Silicate Solutions, Alum Concentration and Coagulating Power

	Alum p.p.m.	SiO_2 p.p.m.	Age Hrs.	Minutes Stirring 5	10	15	pH	Alk.
1.	4	3.7	2	none	fine	fine		
2.	10	3.7	2	large	extra large	extra large	6.9	36
3.	4	3.7	54	none	very fine	very fine		
4.	10	3.7	54	medium	large medium	large medium	6.9	36
5.	4	3.7	0	none	none	none		
6.	10	3.7	0	none	none	none	6.9	38

$Ca(HCO_3)_2$ Alkalinity 42 Turbidity 30 Temperature 24°C

Baylis (15) conducted a large number of his experiments on Lake Michigan water. For this reason I decided to try tap water instead of prepared distilled water. The disadvantage in using tap water or natural water is the fact that such waters may not remain constant in chemical composition from day to day. This is especially true in Stillwater where we have five sources of supply. However, tap water has one advantage in that it enables one to more nearly duplicate plant conditions.

Table VIII shows the effect of using tap water instead of prepared distilled water on aluminum hydroxide coagulation. Both the aluminum sulfate and sodium silicate concentrations were held constant. The time of aging was varied. In the case of 6 Merck's sodium silicate was used instead of Sargent's.

TABLE VIII

Effect of Using Tap Water on the Size of the Coagulated Particles

	Alum p.p.m.	SiO_2 p.p.m	Age Hrs.	Minutes Stirring 5	10	15	20
1.	0	0	--	none	none	none	none
2.	8	0	--	large	large	large	large
3.	8	3.7	72	medium	large	large	large
4.	8	3.7	10	large	large	extra large	extra large
5.	8	3.7	10	large	large	extra large	extra large
6.	8	3.7	10	fine	low medium	medium	large

Tap Water Alkalinity 90 Turbidity 30 Temperature 24

Table IX further shows the effect of age of sodium silicate solutions with constant aluminum sulfate concentration. Solution 6, in which the sodium silicate had aged only 30 minutes showed the largest sized particles. The pH of the 6 different solutions remained constant at 7.6.

TABLE IX

Effect of Age of Sodium Silicate Solutions as an Aid to Coagulation

	Alum p.p.m.	SiO_2 p.p.m.	Age Hrs.	Minutes Stirring 5	10	15	20	pH
1.	0	0	--	none	fine	fine	medium	7.6
2.	10	1.8	56	fine	fine	fine	medium	7.6
3.	10	3.7	56	very fine	very fine	very fine	very fine	7.6
4.	10	1.8	24	fine	fine	medium	medium	7.6
5.	10	3.7	24	very fine	very fine	fine	medium	7.6
6.	10	3.7	15	very fine	low medium	lrg. med.	large	7.6

$Ca(HCO_3)_2$ Alkalinity 34 Turbidity 30 Temperature 24

The purpose of the work shown in Table X was to determine if boiling silicate solutions of different ages had any effect on their coagulating power. The solutions were boiled for 90 minutes then tested in the usual manner for coagulation. Boiling seems to increase the power of the sodium silicate solutions to aid coagulation. In No. 6 the sodium silicate solution had no H_2SO_4 in it.

TABLE X

Relationship Between Time of Boiling of Silicate Solutions and Coagulation

	Alum p.p.m.	SiO_2 p.p.m	Age Hrs.	Boiled Minutes	Minutes Stirring 5	10	15	20	25
1.	10	0	0	0	very fine	fine	low med	medium	medium
2.	10	3.7	12	0	very fine	fine	low med	medium	medium
3.	10	3.7	12	90	fine	low med	lrg med	lrg med	lrg med
4.	10	3.7	84	0	fine	lrg med	large	large	large
5.	10	3.7	84	90	fine	low med	lrg med	large	large
6.	10	3.7	--	0	fine	low med	low med	low med	low med

$Ca(HCO_3)_2$ Alkalinity 34 Temperature 24°C Turbidity 30

CHAPTER III

Relation Between Apparent Silica Content as Measured by Colorimeter and Age of Sodium Silicate Solutions

The purpose of the work reported in this chapter is to show the correlation between the molybdate test for silica, the age of the silicate solutions and their coagulating value. The gravimetric analysis of the sodium silicate was checked colorimetrically with the molybdate reagent to see if the standard potassium chromate solution was correct (23). A Dubasq colorimeter was used to aid in distinguishing the yellow color developed when silica is present. Table XI is correlated with the development of maximum aid to coagulation.

TABLE XI

Correlation Between Age and Apparent SiO_2 Content of Sodium Silicate Solutions

Standard	Time Minutes	Sample	Apparent SiO_2
20	15	14.2	70.4
20	35	12.8	78.1
20	50	11.4	87.7
20	70	11.4	87.7
20	90	11.4	87.7
20	120	11.4	87.7

A graphical representation of the preceding data is presented in Figure 1.

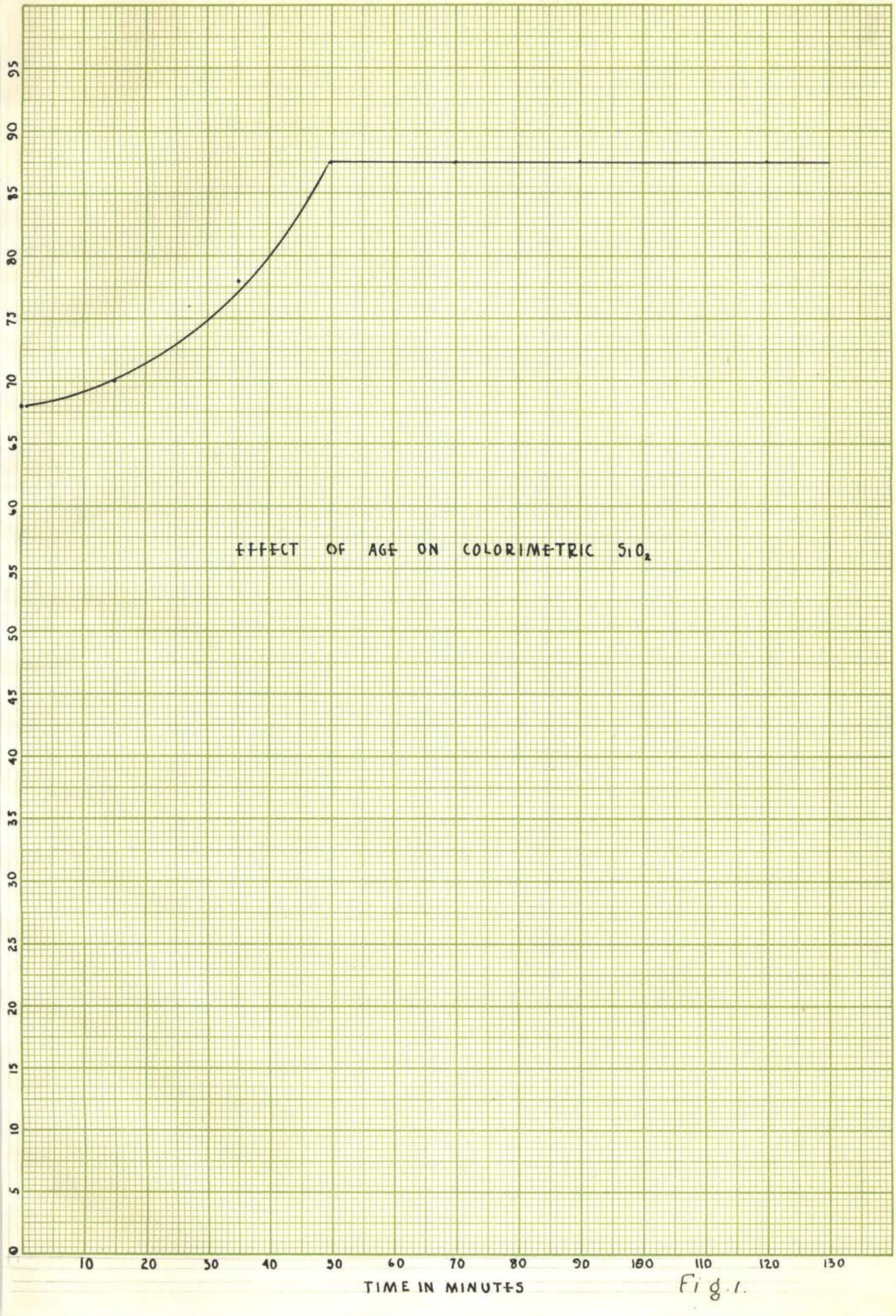

EFFECT OF AGE ON COLORIMETRIC SiO_2
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME IN MINUTES

Fig. 1.

In Table XII the sodium silicate solutions were boiled and tested at fifteen minute intervals for SiO_2 content for a period of one hour. After boiling for one hour the SiO_2 content became constant. The amount of SiO_2 increases with time of boiling.

TABLE XII

Relation Between Temperature and Colorimetric Silica Content

Boiling Minutes	Standard	Sample	Apparent SiO_2 p.p.m.
0	20	14.5	68.9
15	20	13.3	75.2
30	20	12.6	79.3
45	20	12.4	80.6
60	20	12.3	81.6

Figure 2 plots time against SiO_2 content giving the smooth curve as represented. When the solutions were boiled there was a tendency for the yellow color to develop before the addition of the hydrochloric acid.

Table XIII represents the correlation between time of boiling and the coagulating power. I tried raising the temperature of the solution just to the boiling point to see if it had any effect. The results were negative as shown below. After 30 minutes boiling, the sodium silicate solutions show considerable improvement in their ability to aid coagulation. At the end of

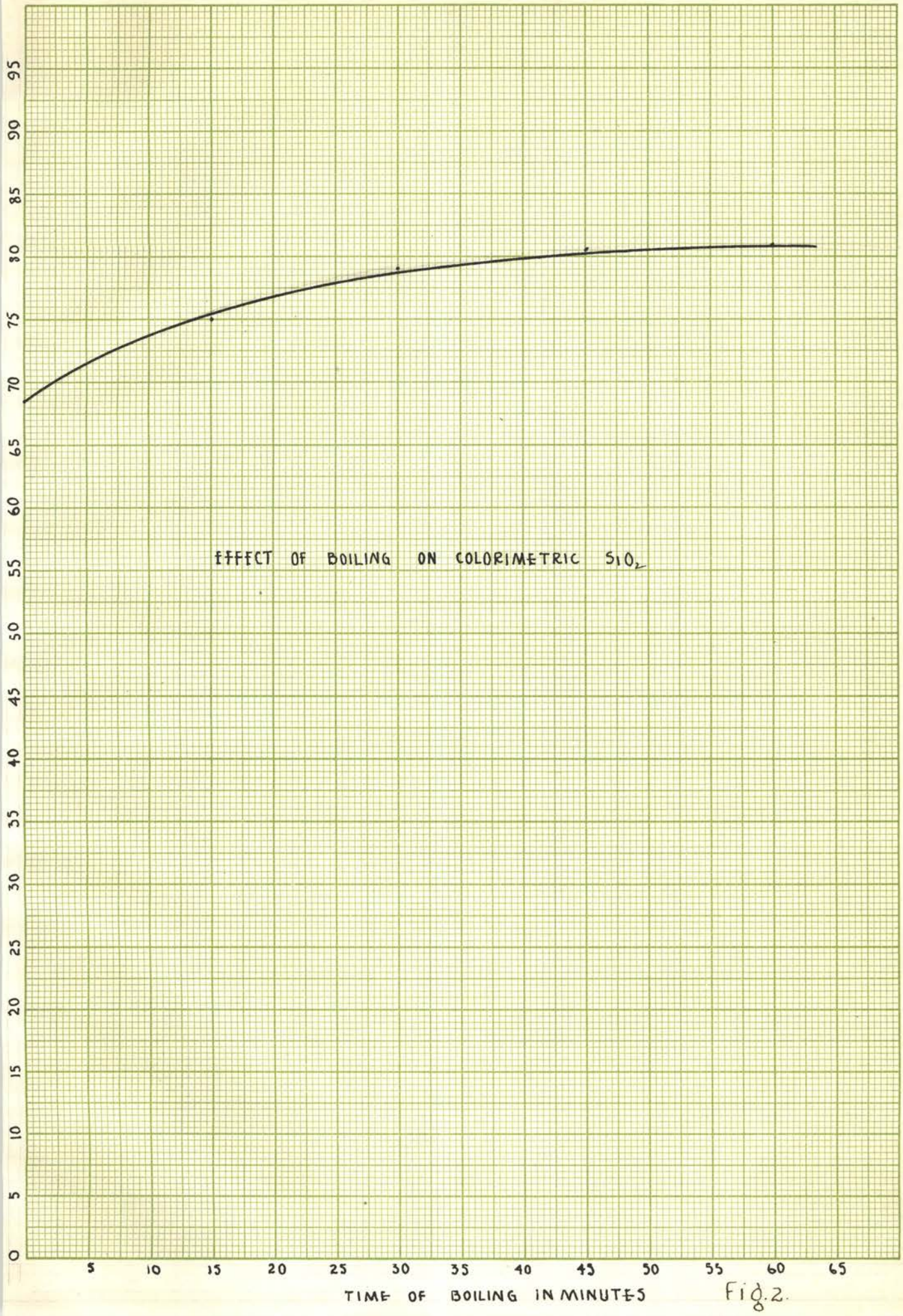

EFFECT OF BOILING ON COLORIMETRIC SiO_2
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
5
10
15
20
25
30
35
40
45
50
55
60
65
TIME OF BOILING IN MINUTES

Fig. 2.

one hour the solutions that had been boiled showed the same efficiency as those that had not been boiled.

TABLE XIII

Relation Between Time of Boiling and Ability to Aid Coagulation

	Alum p.p.m	SiO_2 p.p.m	Age Min.	Boiled Min.	Minutes Stirring 5	10	15
1.	0	0	0	0	none	none	none
2.	8	0	0	0	fine	medium	large
3.	8	3.7	10	0	medium	large medium	large
4.	8	3.7	10	1	low med	large medium	large
5.	8	3.7	15	0	medium	large medium	large
6.	8	3.7	15	15	large med	large medium	large
7.	8	3.7	30	0	medium	large medium	large
8.	8	3.7	30	30	large	immense	immense
9.	8	3.7	45	0	medium	large	extra large
10.	8	3.7	45	45	medium	extra lrg	immense
11.	8	3.7	60	0	extra lrg	immense	immense
12.	8	3.7	60	60	extra large	immense	immense

$Ca(HCO_3)_2$ Alkalinity 34 Temperature 24 Turbidity 30

CHAPTER IV

Influence of Dialysis on Silica Content

The purpose of the work reported in this chapter is to determine the effect of dialysis and the resulting coagulating power. Collodion bags were made by pouring collodion into a 250 ml. round bottom flask, drying and removing the bag. The bags were filled with distilled water and allowed to stand in distilled water for several hours to remove the last traces of ether. Fifty ml. of sodium silicate solution were then placed inside each bag and the bag hung in 500 ml. of distilled water. After dialyzing for a definite length of time the bags were removed and the contents analyzed colorimetrically for SiO_2. The SiO_2 inside the bag and that which passed through the bag was tested for its ability to aid coagulation.

Table XIV shows the SiO_2 which passed through the bag gave no aid to coagulation. The SiO_2 that passed through the bag was boiled for thirty minutes and then tested for aid to coagulation. No aid, however, was obtained.

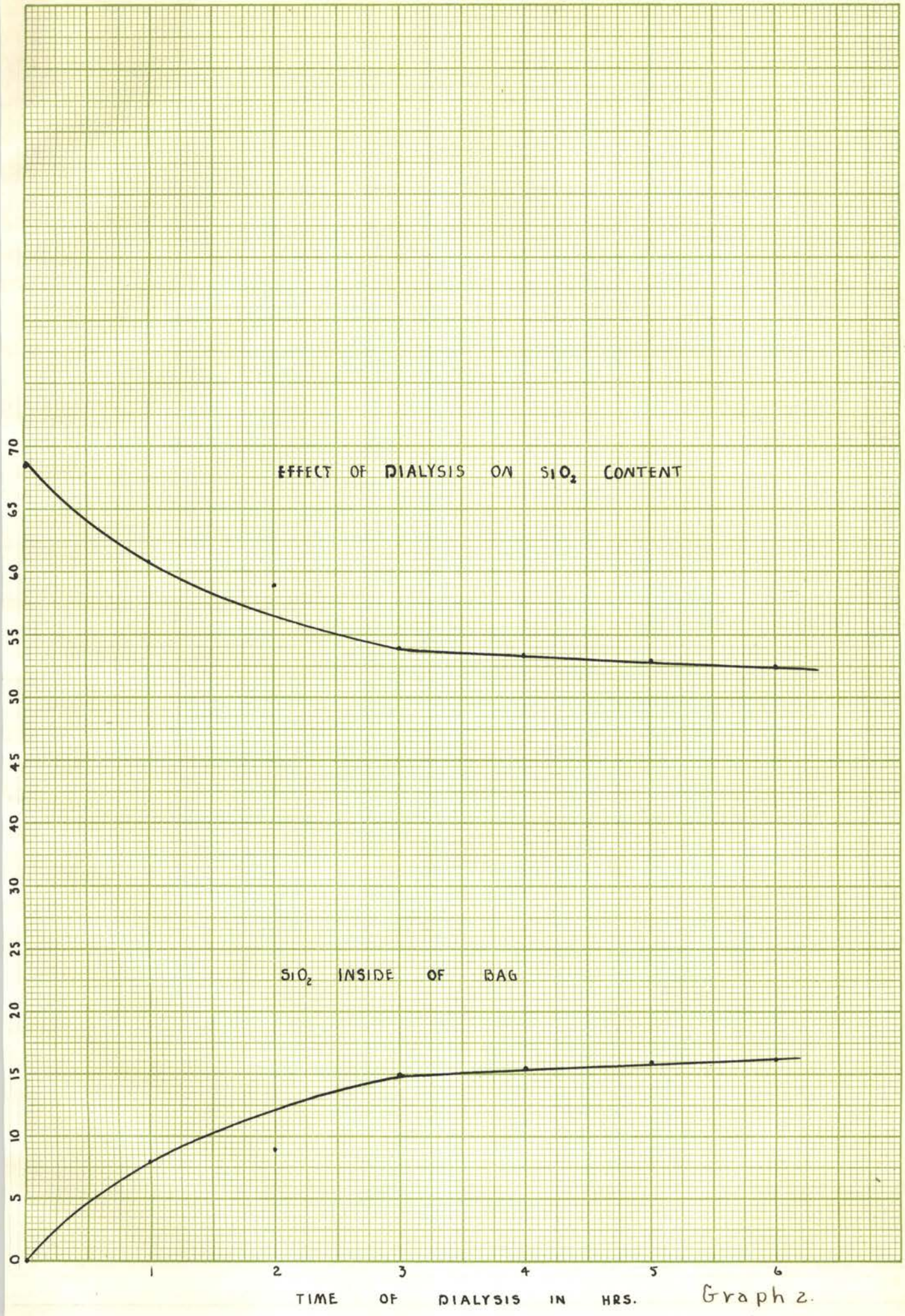
TABLE XIV

Relation Between Dialysis and Ability to Aid Coagulation

Dialyzed Hrs.	SiO_2 in Bag	Effect on Coagulation	SiO_2 in water p.p.m.	Effect on Coagulation
1	61	aids	8	no aid
2	59.7	aids	9.3	no aid
3	54	aids	14.8	no aid
4	53.4	aids	15.3	no aid
5	53.1	aids	15.6	no aid
6	52.7	aids	16.1	no aid

Graph 2 is a representation of the above data.

Dialysis was carried on also in days. I found that after one day the amount of SiO_2 which passed through the bag was approximately equal to the amount that was left behind. At the end of the ninth day the amount of silica inside the bag was 34.5 p.p.m. while the silica that passed through the bag gave only slight aid to coagulation, indicating that the form of silica which aids coagulation is a colloidal form.


EFFECT OF DIALYSIS ON SiO_2 CONTENT
SiO_2 INSIDE OF BAG
0
5
10
15
20
25
30
40
45
50
55
60
65
70
1
2
3
4
5
6
TIME OF DIALYSIS IN HRS.

Graph 2.

CHAPTER V

The purpose of the work reported in this chapter is to find out whether sodium silicate in the concentrations used will adsorb a dye, and to learn if sodium silicate solutions show a Tyndall effect or ultramicroscopic effect. If the solutions show an ultramicroscopic effect then the charge on the ion can be determined by cataphoresis. No particles could be observed in the ultramicroscope.

Methylene blue was used as a typical dye for the adsorption effect. A very small amount of the methylene blue was added to the sodium silicate solutions containing aluminum hydroxide and stirred for about 45 minutes. Then the resulting solution was examined to see if the intensity of the blue color had decreased. No change in color could be detected.

The sodium silicate solutions were next examined to see if they showed a Tyndall effect. This was done by placing a quantity of the solution in a round bottom flask and holding it up towards the sun. No particles could be observed. By holding it in front of a strong carbon arc light no effects were observable.

CONCLUSIONS

1. A pH of 7.2 has been confirmed to be the best for coagulation experiments.
2. Sodium silicate solutions develop their maximum aid to coagulation in the course of one hour.
3. Contrary to Baylis' work, the sodium silicate solution continues to aid coagulation after 24 hours.
4. When sodium sulfate was used in the absence of the silicate ion, no aid to coagulation was obtainable. This proves that the aid was due to the sodium silicate.
5. The effect of boiling solutions of sodium silicate is to increase the speed of reaction, or their power to aid coagulation, to a certain extent.
6. The form of silica that aids coagulation is colloidal.
7. The following equilibrium exists:

$$SiO_2 \times H_2O \rightleftharpoons SiO_2 \times H_2O$$

crystalloid colloid

BIBLIOGRAPHY

1. Mellor "Comprehensive Treatise of Inorganic Chemistry." Vol. 6, Longman Green and Co., 1925.
2. Dienert and Wandenbulke, Comp. Rend. 176 1478 (1923)
3. Dienert and Wandenbulke, Bull. Soc. Chem. 33 1131 (1923)
4. Harman, R. W. J. Phys. Chem. 29 1155-68 (1925)
5. Harman, R. W. J. Phys. Chem. 30 359-68 (1926)
6. Harman, R. W. J. Phys. Chem. 30 1100-11 (1926)
7. Harman, R. W. J. Phys. Chem. 30 917-24 (1926)
8. Harman, R. W. J. Phys. Chem. 31 511-18 (1927)
9. Pastma, J. Rec. trav. Chem. 51 726-38 (1932)
10. Baschieri, E. Atti. Soc. Tosc. sci. Nat. Proc. Verb .13 No. 5
11. Grundman, W. Kolloid Z. 36 328-31 (1925)
12. Inaba, I. Sci. Papers Inst. Phys. Chem. Research 15 277-87 (1931)
13. Daelter, C. Rec. trav. Chem. 42 729-32 (1923)
14. Baylis, J. Journal Am. Water Works Assn. 1355 Sept. '37
15. Baylis, J. Water Works and Sewage 469 June '36
16. Baylis, J. Water Works and Sewage 61 Feb. '37
17. Baylis, J. Water Works and Sewage 221 June '37
18. Peterson, H., & Bartow, E. Ind. & Engr. Chem. 20 51 (1928)
19. Black, Rice and Bartow, Ind. & Eng. Chem. 25 811 (1933)
20. Smith, O. M., J. Am. Chem. Soc. 42 460-72 (1920)
21. Smith, O. M., Jour. A. W. W. A. 11 : 302 (1920)
22. Guthier and Brintzinger, Z. Anorg. Chem. 140-61 (1918-19)
23. Standard Methods of Water Analysis, Eighth Edition, American

Public Health Association, 1936.

24. Treadwall-Hall, Analytical Chemistry, Vol. II

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I, Foster Darrell Roach, was born near Van Buren, Arkansas, November 5, 1915. I received my grade school education in the Van Buren Public schools and was graduated from the Van Buren High School in May 1932. I entered the University of Arkansas at Fayetteville, Arkansas, in September, 1932, and was granted the degree of Bachelor of Science in June, 1936. I entered the Graduate School of Oklahoma Agricultural and Mechanical College in September, 1936, as a graduate assistant in the Department of Chemistry. The requirements for the degree of Master of Science will be completed in May, 1938.

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